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Martin Pomerantz, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick

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FIELD	GROUP	SUB-GROUP	Poly(di-2-thienyl-2,5-dialkoxy-p-phenylene); polypyrrole; hydrazine, sensory Kevlar polyelectrolyte; Raman spectroscopy; band structure calculations

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Symmetrically and unsymmetrically substituted poly(di-2-thienyl-2,5-dialkoxy-p-phenylenes) have been prepared and studied. X-ray studies have shown that the unsymmetrically substituted polymer is completely amorphous while the symmetric polymer exhibits a high level of crystallinity. The dihexadecyloxy derivative has been observed to be birefringent and, after NO_2PF_6 doping, a film of this polymer shows a conductivity of 300 S/cm^{-1} . A water soluble benzylsulfonate derivative of Kevlar has been prepared and a polypyrrole film formed with this as the electrolyte shows a conductivity of ca. 10 S/cm^{-1} . Poly-pyrrole/naphthalene sulfonate thin films can be used to detect ppb quantities of hydrazine in the presence of ammonia. A new technique which combines cyclic voltammetry with Raman scattering has been developed. Vibrational absorptions as a function of electrode potential can be monitored. Detailed conformational analyses for monomers and band structure calculations for polymers have been carried out on substituted pyrrole-phenylene-pyrrole systems.

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Technical Report No. 24

Electronic and Ionic Transport in Processable Conducting Polymers

by

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Description of Progress

The symmetrically substituted poly(di-2-thienyl-2,5-didodecyloxyphenylene) and unsymmetrically substituted poly(di-2-thienyl-2-dodecyloxy-5-methoxyphenylene) have been studied, after annealing, by X-ray diffraction in a collaborative program with researchers at the Naval Air Development Center. While the unsymmetrically substituted polymer is completely amorphous, the symmetrically substituted polymer exhibits a high level of crystallinity. The symmetrically substituted poly(di-2-thienyl-2,5-dihexadecyloxyphenylene) has been synthesized and shown to be birefringent in the melt. Annealing of this polymer has been shown to improve mechanical integrity after NO_2PF_6 doping, with free-standing films exhibiting conductivities up to $3 \Omega^{-1} \text{ cm}^{-1}$.

Poly(*p*-phenyleneterephthalamido benzylsulfonate) (PPTA-BZS) has been synthesized to yield a water soluble polyelectrolyte derivative of Kevlar that contains aromatic sulfonates. The PPTA-BZS has been used as the electrolyte for the electropolymerization of pyrrole and free-standing films having conductivities of *ca.* $10 \Omega^{-1} \text{ cm}^{-1}$ have been prepared.

Chemical reduction of polypyrrole/naphthalene sulfonate thin films by hydrazine and sulfite has been studied with a view to exploring chemical sensor applications. Detection limits of ppb have been established and selectivity to hydrazine in the presence of ammonia has been established. *In situ* Raman spectroelectrochemical studies have also been completed on polypyrrole, and a novel combined cyclic voltammetry-Raman scattering technique ("CV-Raman", no pun intended!) has been developed. It is shown how Raman monitoring of a probe vibrational peak as a function of electrode potential reveals features not readily apparent in conventional CV. Studies also continue on copper macrocycle binding in chemically modified electrodes.

Detailed conformational analyses have been performed for polymers derived from a pyrrole-phenylene-pyrrole monomeric unit, with various substituents (e.g., CH_3 or OCH_3) on the central phenylene. Band structure calculations have also been performed. This work is now being extended to similar furan and thiophene systems.

Attempts to prepare an alkoxy substituted thienc[3,4-b]pyrazine as a low band gap conducting polymer have thus far been unsuccessful. Work on low band gap systems is continuing.

Publications

Papers Published

Jolly, C. A. and Reynolds, J. R. "Mechanically Durable, Semiconducting and Optically Polarizing Poly(nickel tetrathiooxalate)/Poly(vinyl alcohol) Composites," *Chem. of Materials* **1990**, 2, 479-480.

Papers in Press

Reynolds, J. R. and Pomerantz, M. "Processable Electronically Conducting Polymers," in *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York; Vol. 2, Chapter 4, pp. 187-256, in press.

Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Marynick, D. S., and Nayak, K. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Bithiophene Repeat Units," *Macromolecules*, in press.

Sundaresan, N. S.; Reynolds, J. R., and Ruiz, J. P. "Photocurrent Response of Poly(3-ethylmercaptothiophene)," *J. Mat. Sci.*, in press.

Qiu, Y. J. and Reynolds, J. R. "Dopant Anion Controlled Ion Transport Behavior of Poly-pyrrole," *Polym. Eng. and Sci.*, in press.

Basak, S.; Rajeshwar, K., and Kaneko, M. "In Situ Photogeneration of a Catalyst on a Chemically-Modified Electrode Surface: Application to a Mixed Valent Hexacyanoferrate System," *J. Electroanal. Chem.*, in press.

Reynolds, J. R. and Pomerantz, M. "The International Conference on Science and Technology of Synthetic Metals," *ESN Information Bulletin* (ONR European Office), in press.

Papers Submitted for Publication

Baker, C. K. and Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites," *J. Phys. Chem.*, submitted for publication.

Stickle, W. F.; Reynolds, J. R., and Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(Vinyl Alcohol) Composites," *Langmuir*, submitted for publication.

Wang, F.; Qiu, Y. J., and Reynolds, J. R. "Synthesis and Characterization of Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes," *Macromolecules*, submitted for publication.

Qiu, Y. J. and Reynolds, J. R. "Charge and Ion Transport in Poly(pyrrole copper phthalocyanine-sulfonate) During Redox Switching," *J. Electroanal. Chem.*, submitted for publication.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J., and Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends," *Synth. Met.*, submitted for publication.

Prezyna, L. A.; Wnek, G. E.; Qiu, Y. J., and Reynolds, J. R. "Interaction of Cationic Poly-peptides with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(N-methylpyrrole)/Poly(styrene sulfonate)," *Macromolecules*, submitted for publication.

Reynolds, J. R.; Ruiz, J. P.; Nayak, K.; Child, A. D., and Marynick, D. S. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Heterocycle Repeat Units," *Synth. Met.*, submitted for publication.

Prezyna, L. A.; Wnek, G. E.; Lee, J. J.; Reynolds, J. R., and Qiu, Y. J. "Interaction of Cationic Proteins with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(N-methylpyrrole)/Poly(styrene sulfonate) Films," *Synth. Met.*, submitted for publication.

Krishna, V.; Ho, Y.-H.; Basak, S., and Rajeshwar, K. "A Luminescence Probe and Voltammetry Study of Ion Transport During Redox Switching of Polypyrrole Thin Films," *J. Am. Chem. Soc.*, submitted for publication.

Papers Acknowledging DARPA Support for Instrumental Purchases

Pomerantz, M. and Levanon, M. "Bis(dimethyl Malonato)ketazine. Formation and Inversion/Rotation Barrier," *Tetrahedron Lett.* **1990**, *31*, 4265.

Pomerantz, M. and Levanon, M. "Carbene Addition to the 2,3-Bond of Naphthalene and Thermal Wolff Rearrangement of Bis(methoxycarbonyl)carbene," *Tetrahedron Lett.*, in press.

Meetings Attended and Papers and Talks Presented

John Reynolds attended the American Chemical Society Polymer Division 15th Biennial Polymer Symposium, November 1990, in Fort Lauderdale, Florida, and presented the following paper:

Reynolds, J. R.; Gieselman, M. B.; Qiu, Y. J., Pyo, M. H.; Wnek, G. E., and Prezyna, L. A. "Electrically Conductive and Electroactive Polyheterocycle/Polyelectrolyte Molecular Composites."

John Stenger-Smith of the Naval Weapons Center presented the following paper at the same meeting on a collaborative project:

Stenger-Smith, J. D.; Reynolds, J. R., and Tanaka, S. "Synthesis and Characterization of a New Conjugated Polymer: Poly(2,5-(4'-Methoxy)Stilbenylene Vinylene) Prepared from a Cycloalkylene Sulfonium Salt Precursor Polymer."

John Reynolds, Krishnan Rajeshwar and graduate student Melinda B. Gieselman attended the American Chemical Society combined Southeast-Southwest regional meeting, December 5-7, 1990, and presented the following papers:

Reynolds, J. R. and Qiu, Y. J. "Controlled Ion Transport in Polypyrrole During Redox Switching."

Reynolds, J. R. and Gieselman, M. B. "Synthesis and Characterization of New Polyelectrolyte for Application in Polypyrrole Composites."

Rajeshwar, K. "Charge Transport/Storage in Biconductive Oxides and Polymers."

Visitors to The University of Texas at Arlington

Professor M. J. Weaver, Purdue University, visited on October 19, 1990, and presented a seminar entitled "Dynamical Factors in Electron-Transfer Processes."

Professor Patrick Cassidy, Southwest Texas State University, visited on November 2, 1990, and presented a seminar entitled "Recent Developments in Condensation Polymers Containing the Hexafluoroisopropylidene Unit."

Dr. Leonard Buckley, Naval Air Development Center, Warminster, Pennsylvania, visited on November 8, 1990, and presented a seminar entitled "Nonlinear Optical Polymers: Material for In-Situ Sensors," and discussed ongoing research programs at NADC.

Dr. Tomas A. Pajkossy, Hungarian Academy of Sciences, visited on November 9, 1990, and presented a seminar entitled "Fractal Electrochemistry."

Professor Karl Kadish, University of Houston, visited on November 30, 1990, and presented a seminar entitled "Chemistry and Electrochemistry of Metalloporphyrins."

Personnel Changes

Dr. Benjamin Chaloner-Gill, Ph.D. from the University of Rhode Island, has joined our group as a Postdoctoral Associate.

Jimmy Rogers has joined our group as a graduate research assistant.

Dr. Susumu Tanaka, Postdoctoral Associate, has returned to the Research Institute for Polymers and Textiles, Tsukuba, Japan.

New Funding/Collaborations

LTV Aerospace and Defense Co., "Conducting Polymers," 1990, \$2,400.00.